

# The Solvation of Polar Molecules in Organic Solvents

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## Abstract

The solvent induced frequency shift (SIFS) for four aprotic solvents, namely, acetonitrile, acetone, dimethyl sulfoxide, and propylene carbonate as dilute solutes was determined in a wide range of organic solvents, both polar and non-polar, protic and aprotic. It is shown that the most important parameter determining the magnitude of the shift is the ability of the solvent to interact with the solute as a Lewis acid. The direction of the shift depends on the nature of the solvent and the band chosen for study. Although these studies usually involve the vibrational mode directly associated with the electronegative polar group in the given molecule, there are often other modes which give a stronger correlation with solvent acidity. These observations are discussed with respect to the role of dipole-dipole interactions in determining the structure of polar aprotic liquids.

## Introduction

Vibrational spectroscopy provides a powerful tool for studying the intermolecular interactions of polar aprotic solvents. These solvents are characterized by high relative permittivities but also by high viscosities. The former feature makes them attractive systems for use in high energy density batteries which make use of very reactive metals such as lithium [1]. On the other hand, the high viscosity means that electrolytes dissolved in aprotic solvents are characterized by poor conductivity. As a result most practical systems are based on solvent mixtures with lower permittivity and lower viscosity.

Polar aprotic solvents have fairly high dipole moments due to the electronegative polar group in the molecule. As a result dipole-dipole interactions are very strong in the pure liquid and lead to significant dimerization or aggregate formation. The strong intermolecular forces are precisely the reason why these systems possess high viscosities. The polar group in the molecule also gives the strongest band in the infrared or Raman spectrum of the molecule. The frequency of this band depends on the nature and strength of the intermolecular interactions involving the electron rich polar group. Thus, when the aprotic solvent is dissolved as a dilute solute in another solvent, the solvent induced frequency shift (SIFS) may be used to characterize the intermolecular interactions [2]. SIFS involving the principal infrared band have been studied in a number of aprotic solvents including acetonitrile [3,4], acetone [5,6], benzonitrile [3], dimethyl sulfoxide [7], nitrobenzene and nitromethane [8], propylene carbonate [9], and tetramethylurea [10].

Examination of the main band due to the polar group in the IR spectrum of the pure aprotic solvent reveals that it has a complex nature due to strong associative effects [6,11,12]. Thus, one usually finds bands in this region due to solvent monomers, dimers, and other aggregates even when the aprotic molecule is a dilute solute in another solvent. Thus, it is often preferable to examine other bands in the spectrum of the aprotic molecule which also display a SIFS but which are less affected by the formation of molecular aggregates.

In the following paper, the SIFS observed in four aprotic solvents namely acetonitrile (AcN), acetone (AC), dimethyl sulfoxide (DMSO) and propylene carbonate (PC) which have been studied in this laboratory are reviewed. The molecular properties which determine the magnitude of the SIFS are presented, and the correlations observed between the SIFS and these properties are discussed.

### The Solvent Parameters

The SIFS is assumed to be due to one or more properties of the solvent so that the frequency of a given band can be described as

$$\nu = \nu_o + \sum_i \alpha_i P_i \quad (1)$$

where  $\nu$  is the frequency of the band observed in a given solvent,  $\nu_o$ , the value of the frequency in a completely non-interacting solvent,  $P_i$ , the value of the  $i$ th property, and  $\alpha_i$ , the coefficient describing the response of the band to that property. Equation (1) is a generalized form of an equation originally proposed by Koppel and Palm [13]. The coefficients  $\alpha_i$  are obtained using multiple linear regression analysis. The procedure used is to test each of the parameters in a simple linear regression and to select the parameter which describes most of the variation in  $\nu$ . Then each of the remaining parameters is tested in a two parameter linear regression, the best of these being selected as the second parameter. This procedure is continued using the usual statistical criteria to determine whether addition of another parameter to the description is valid or not. Further details of the procedure used in the analysis is given elsewhere [2,14].

The parameters tested in the analysis include two which measure specific molecular properties of the solvent and two which relate to the properties of the solvent as a dielectric continuum [2,14]. Studies of solvation in these systems have shown that the acidity and basicity of the solvent are important molecular properties. The effectiveness of a given solvent as a Lewis acid or base can only be estimated on the basis of empirical scales. Those chosen here on the basis of a detailed examination of solvation effects involving both ions and polar molecules

are the Gutmann donor number DN [15] for solvent basicity and the Gutmann acceptor number AN for solvent acidity [16]. Detailed arguments for the choice of these scales were given in earlier work [2,14]. The solvation parameters which are based on bulk dielectric properties are solvent polarity  $Y$  and solvent polarizability  $\Pi$ . The first is defined on the basis of the Debye equation as

$$Y = (\epsilon_s - 1)/(\epsilon_s + 2) \quad (2)$$

where  $\epsilon_s$  is the static relative permittivity of the pure solvent. The polarizability comes from the Lorentz-Lorenz equation so that

$$\Pi = (n_{op}^2 - 1)/(n_{op}^2 + 2) \quad (3)$$

where  $n_{op}$  is the refractive index of the solvent in the visible region. The use of these four parameters follows the Koppel and Palm analysis [13].

Values of the solvent parameters together with the static relative permittivity  $\epsilon_s$  and the molecular dipole moment  $p$  are given in Table 1 for a wide range of organic solvents. When a large number of solvents are involved these parameters are not linearly related.

The solvents considered here fall into three groups. The first group contains protic solvents which can interact with a Lewis base via hydrogen bonding. They are reasonably strong Lewis acids as reflected by the high value of the acceptor number AN. The polarity of the solvent varies considerably among those used in the present experiments. The protic amides, formamide and N-methyl formamide have very high relative permittivities, and therefore, high values of the polarity  $Y$ . Most of the protic solvents have intermediate values of  $Y$ . The basicity of protic solvents cannot be determined using the method originally devised by Gutmann [15]. However, alternative techniques have been devised to estimate solvent donicities [14] and they are reported here on the Gutmann scale. Most protic solvents including water are Lewis bases of intermediate strength.

The second group of solvents contains aprotic polar solvents which possess high dipole moments due to the presence of an electronegative polar group. These solvents are usually strong Lewis bases and weak Lewis acids. The latter feature follows from the fact that there is no part of the molecule which can act chemically as a Lewis acid. Thus, stabilization of strong Lewis bases such as anions in aprotic solvents results only from the negative end of the dipole in the molecule. The further this is from the positive end, the poorer the solvent is as a Lewis acid. The Lewis basicity of the solvent varies considerably with the nature of the polar group in the solvent. Thus, the nitro group in nitromethane and nitrobenzene is a poor Lewis base whereas the S=O group in DMSO is a strong Lewis base. There is also no connection between solvent polarity and basicity. Thus, the three solvents, acetonitrile, dimethylformamide and nitromethane have approximately the same polarity but very different basicities.

The last group considered is non-polar aprotic systems. These systems are usually poor Lewis acids and bases. Solvation is often due to the solvent's polarizability, for example, as in the case of benzene. However, there are small differences between these systems which makes their inclusion in a detailed study worthwhile.

## Experimental

Spectra were collected using the Mattson Research Series FTIR spectrometer with a resolution of  $0.5\text{ cm}^{-1}$ . All experiments were carried out at  $22^{\circ}\text{C}$ . The solvents used were HPLC grade, at least 99.9% pure with a residual water level less than 0.005%. Solutions were made up with a constant molar ratio of 1 mole of solution to 12 moles of solvent. They were handled in a dry box under a nitrogen atmosphere to prevent contamination by water. The spectra were analyzed by subtracting the spectrum of the pure solvent from that of the solution. The multiplying factor used in subtraction was chosen to minimize solvent features in a spectral region where the solute did not absorb. The data were analyzed using Peak Fit software.

## Results

The studies carried out involved solvents from all three groups. In the analysis presented here for AcN only polar solvents were considered. The SIFS for this solvent is much smaller than for the others and a satisfactory analysis was not possible when non-polar solvents were included. Previous reports for AcN [4] and DMSO [7] included trifluoroacetic acid as a solvent which is a very strong Lewis acid. These data were not considered here simply because this solvent has properties which are very different from the majority of those considered. Otherwise, omission of the data for trifluoroacetic acid from the analysis had a negligible effect on the results obtained.

Acetonitrile (AcN) is not a strong Lewis base. It has a strong band in the infrared at  $2253\text{ cm}^{-1}$  due to the  $\text{C}\equiv\text{N}$  stretch ( $\nu_2$ ). In a previous study it was shown that the frequency of this band is shifted to higher frequencies in the presence of stronger Lewis acids [4]. On the other hand in the presence of stronger Lewis bases, the  $\text{C}\equiv\text{N}$  band is shifted to lower frequencies. The changes are not large. In the presence of acetic acid,  $\Delta\nu_2$  is  $12.0\text{ cm}^{-1}$ , and in the presence of hexamethylphosphoramide,  $-5.5\text{ cm}^{-1}$ .

When the SIFS for the  $\nu_2$  band of AcN in 18 polar solvents are considered together a weak correlation with the solvent's acceptor number is found, namely

$$\nu_2 = 2246.7 + 0.314AN \quad (4)$$

with a standard deviation of 2.7 and a correlation coefficient of 0.825. The fit is considerably improved by adding the solvent polarity  $Y$  to the description of the solvent effect. The result is then

$$\nu_2 = 2273.2 + 0.226AN - 27.2Y \quad (5)$$

with a standard deviation of 1.89 and a correlation coefficient of 0.924. A further improvement is found where the DN is added as a third parameter with the result

$$\nu_2 = 2272.8 + 0.227AN - 24.4Y - 0.109DN \quad (6)$$

The standard deviation is reduced to 1.66 and the correlation coefficient is 0.946. The role of the individual parameters is found by calculating partial regression coefficients. Thus, the solvent acidity accounts for 48 percent of the explained variation in  $\nu_2$ , the polarity for 35 percent, and solvent basicity for 17 percent. The excellent quality of the fit is illustrated in Figure 1 where the value of  $\nu_2$  estimated by equation (6) is plotted against the experimentally observed value.

AcN is unique among the aprotic solvents considered in that interaction of the polar-C $\equiv$ N group with a strong Lewis acid leads to a blue shift in the frequency of the C $\equiv$ N stretching mode. This is attributed to interaction of the Lewis acid with an antibonding orbital associated with this part of the molecule. On the other hand when AcN interacts with a strong Lewis base such as DMSO or hexamethylphosphoramide, the  $\nu_2$  band is shifted in the red direction. Since a Lewis base is expected to interact with the positive end of the molecular dipole, in this case, the methyl group, this observation suggests that the effect is transmitted through the C-C bond to the -C $\equiv$ N group.

Acetone (AC) is a stronger Lewis base than AcN with a donor number of 17.0. It has a high dipole moment (2.69 Debyes) and is characterized by relatively strong dipole-dipole interactions as a liquid. Careful analysis of the band due to the -C=O stretch ( $\nu_3$ ) shows that there three major components, one due to the acetone monomer, and two due to molecular aggregates [6,11]. The SIFS has been measured for the  $\nu_3$  band due to the monomer in 22 solvents both polar and non-polar. There is a clear correlation between the frequency of this band and the solvent's AN as can be seen in Figure 2. The equation of the least squares fit is

$$\nu_3 = 1718 - 0.286AN \quad (7)$$

with a standard deviation of 1.6 cm<sup>-1</sup> and correlation coefficient of 0.876. When the electron density associated with the C=O group interacts with a Lewis acid, the frequency of the C=O

stretching band is shifted in the red direction. The strongest Lewis acid among the solvents considered is methanol in which  $\nu_3$  is equal to  $1707\text{ cm}^{-1}$ .

The fit to the experimental data is improved somewhat by adding the solvent polarity  $Y$  as a second parameter. The description of the solvent effect is then

$$\nu_3 = 1720 - 0.223AN - 4.77Y \quad (8)$$

with a standard deviation of  $1.3\text{ cm}^{-1}$  and correlation coefficient of 0.917. On the basis of the partial regression coefficients solvent acidity accounts for 69 percent of the explained variation in  $\nu_3$  and solvent polarity for 31 percent.

The effects observed for the C=O stretching mode in AC are complicated by the fact that this part of the molecule is also involved in the formation of dimers and other aggregates. Examination of other spectral features shows that a significant blue shift of the asymmetric stretching band of the molecular skeleton ( $\nu_{17}$ ) is observed with increase in solvent acidity (Figure 3). The equation relating these quantities is

$$\nu_{17} = 1216 + 0.339AN \quad (9)$$

with a standard deviation of  $0.8\text{ cm}^{-1}$  and a correlation coefficient of 0.984 obtained using data in 20 solvents. The correlation is significantly better than the corresponding one for the  $\nu_3$  vibration (equation (7)) and demonstrates that it is better to examine intermolecular interactions using data for a vibrational mode not directly related to the polar group in the molecule. The interesting feature of the observed changes is that the energy associated with this vibration increases as the strength of the interaction between the electron density in the C=O group and the surrounding Lewis acid increases. Finally, no improvement in the correlation was found when other parameters are considered.



DMSO is a much stronger Lewis base than acetone. It has a significantly larger dipole moment (3.96 Debyes) and therefore is expected to have a higher viscosity due to stronger dipole-dipole interactions. In fact, the viscosity of DMSO is more than three times that of AC. From a structural point of view AC and DMSO have exactly the same symmetry properties. Thus, one expects the infrared spectra of these molecules to have the same features.

Examination of the S=O stretching band of DMSO ( $\nu_3$ ) reveals that it has three components, one due to monomers, and the others to aggregates. A plot of the frequency of the monomer band against solvent acidity shows a strong linear correlation (Figure 4). The relationship obtained by least squares analysis using data for 22 solvents is

$$\nu_3 = 1082 - 1.45AN \quad (10)$$

with a standard deviation of  $6.3 \text{ cm}^{-1}$  and a correlation coefficient of 0.947. The negative slope indicates that interaction of a Lewis acid with the electronegative S=O group in DMSO results in a weakening of the bond. The correlation was not improved by adding another solvent parameter to the description of the solvent effect.

Because pure DMSO is strongly dimerized as a result of interactions of the polar S=O group [12], it is interesting to examine the SIFS for other bands in the infrared spectrum. As with acetone, the asymmetric stretching mode of the molecular skeleton ( $\nu_{17}$ ) is particularly useful in this regard. Using data for 21 solvents a strong correlation between the frequency of this band and the solvent acceptor number was found, namely,

$$\nu_{17} = 688.7 + 0.435AN \quad (11)$$

with a standard deviation of  $1.9 \text{ cm}^{-1}$  and a correlation coefficient of 0.949 (Figure 5). As with acetone, the frequency of this band shifts in the blue direction with increase in solvent acidity.

Some improvement in the description of the solvent effect was obtained by adding the donor number to the description as a second independent variable. The relationship is then

$$\nu_{17} = 687.8 + 0.406AN + 0.107DN \quad (12)$$

with a standard deviation of  $1.6 \text{ cm}^{-1}$  and a correlation coefficient of 0.964.

The last aprotic solvent considered is propylene carbonate (PC) which has a very high dipole moment (4.98 Debyes). It is also quite viscous and expected to be highly associated as a pure liquid. Because of its high relative permittivity (66.1) it has been considered a suitable polar solvent for lithium batteries. However, it does not solvate small ions well because it is a moderate Lewis base and a weak Lewis acid. As a result, ion pairing is strong for most soluble electrolytes and electrolytes containing small monoatomic anions such as the chlorides are insoluble. The infrared spectrum of PC is complex because the molecule is not symmetrical. The strongest band is that due to the C=O stretch in the carbonyl group attached to the heterocyclic ring. In addition there are important vibrational modes associated with deformation of the ring [17].

Because of the strong dipole-dipole interactions in PC, one finds three bands in the C=O stretching region at  $1800 \text{ cm}^{-1}$ . One of these is due to the monomers and the other two to molecular associates in the pure liquid. When PC is a dilute solute in another organic solvent, three bands are still observed in this region and care must be taken to select the one which is due to the monomer [9]. This can be determined by following the intensity and position of each band as a function of PC concentration in dilute solutions.

A plot of the frequency of the C=O stretching band ( $\nu_1$ ) for PC as a dilute solute in 24 organic solvents against the solvent's acceptor number is shown in Figure 6. A strong correlation is apparent, which is described by the equation

$$\nu_1 = 1826 - 0.969AN \quad (13)$$

with a standard deviation of  $4.1\text{ cm}^{-1}$  and a correlation coefficient of 0.951. The negative slope demonstrates that the C=O bond becomes weaker when it interacts with a Lewis acid at this end of the molecular dipole. The total change in frequency is large, amounting to  $45\text{ cm}^{-1}$  in the presence of acetic acid, the strongest Lewis acid involved in the data shown in Figure 6.

The description of the SIFS data can be improved when the DN is added as a second parameter to the description of the solvent effect. The equation then is

$$\nu_1 = 1829 - 0.933AN - 0.258DN \quad (14)$$

with a standard deviation of  $3.1\text{ cm}^{-1}$  and a correlation coefficient of 0.974. In this case, 81.1 percent of the explained variation in  $\nu_1$  is due to AN and 18.9 percent to DN.

The SIFS was also examined for the  $\nu_5$  mode which is due to deformation of the heterocyclic ring and occurs at  $1183\text{ cm}^{-1}$  in pure PC. The frequency of this band observed in 24 organic solvents is also strongly correlated with solvent acidity (Figure 7). The equation describing the relationship is

$$\nu_5 = 1176 + 0.374AN \quad (15)$$

with a standard deviation of  $1.5\text{ cm}^{-1}$  and a correlation coefficient of 0.954. In this case, the frequency of the band increases with increase in solvent acidity. No significant improvement in the description of the solvent effect was obtained by adding another solvent parameter from those considered here.

There are several general conclusions that can be reached on the basis of our studies of aprotic solvents. In all cases, the SIFS observed are correlated with the solvent acceptor number demonstrating that the interaction of the electronegative group in the aprotic molecule as a Lewis base is the most important effect to be considered in describing intermolecular forces in

solutions. For AC, DMSO, and PC this is the dominant effect. Consideration of other solvent properties only leads to a small improvement in the description of the solvent effect. However, in the case of AcN for which the SIFS is small, an effective description is not possible on the basis of the AN alone.

All of the solvents considered have a vibrational mode which is directly associated with the electronegative group. Thus, it seems rather obvious that the SIFS should be examined for this mode in order to assess intermolecular interactions. However, the effects observed in this study show that the SIFS for the primary vibrational mode is complicated by the formation of dimers and other molecular associates. When this is the case, there is usually another vibrational mode which also demonstrates a SIFS which does not have these complications.

The final important conclusion is that the most important solvent property in this study, namely, AN, is not related in any way to its bulk properties. Presumably one could estimate solvent acidity and basicity on the basis of a quantum mechanical calculation for the isolated solvent molecule in the gas phase. Unfortunately, this sort of calculation has not been carried out for a wide range of molecules, otherwise considered as solvents in the liquid phase. Since evaluation of acidity and basicity is presently restricted to the use of empirical scales such as those used here, quantum mechanical calculations to elucidate these molecular properties further would be very helpful.

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Table 1. Important Properties of Organic Solvents

	Dipole Moment	Relative Permittivity	Acceptor Number	Donor Number	Polarity	Polarizability
Protic	p / Debyes*	$\epsilon_s$	AN	DN	Y	$\Pi$
Methanol	1.70	32.70	41.3	19.1	0.914	0.202
Ethanol	1.69	24.55	37.1	19.2	0.887	0.220
1-Propanol	1.58	20.33	37.7	19.8	0.870	0.230
2-Propanol	1.66	19.92	33.8	21.1	0.865	0.234
t-Butanol	1.66	12.47	27.1	21.9	0.793	0.234
Benzyl alcohol	1.66	13.1	34.5	15.8	0.801	0.313
Formamide	3.73	111.0	39.8	24.0	0.973	0.267
N-methylformamide	3.83	182.4	32.1	27.0	0.984	0.258
Acetic Acid	1.68	6.15	52.9	12.7	0.634	0.226
Polar Aprotic						
Acetone	2.88	20.7	12.5	17.0	0.868	0.218
Acetonitrile	3.92	35.9	18.9	14.1	0.924	0.211
Benzonitrile	4.18	25.2	15.5	11.9	0.890	0.307

Dimethylacetamide	3.80	37.8	13.6	27.8	0.925	0.261
Dimethylformamide	3.82	36.7	16.0	26.6	0.922	0.257
Dimethylsulfoxide	3.96	46.7	19.3	29.8	0.938	0.283
Hexamethylphosphoramide	5.54	30.0	10.6	38.8	0.910	0.270
Nitrobenzene	4.22	34.8	14.8	4.4	0.918	0.319
Nitromethane	3.46	35.8	20.5	2.7	0.921	0.231
Propylene Carbonate	4.98	66.1	18.3	15.1	0.960	0.250

#### Nonpolar Aprotic

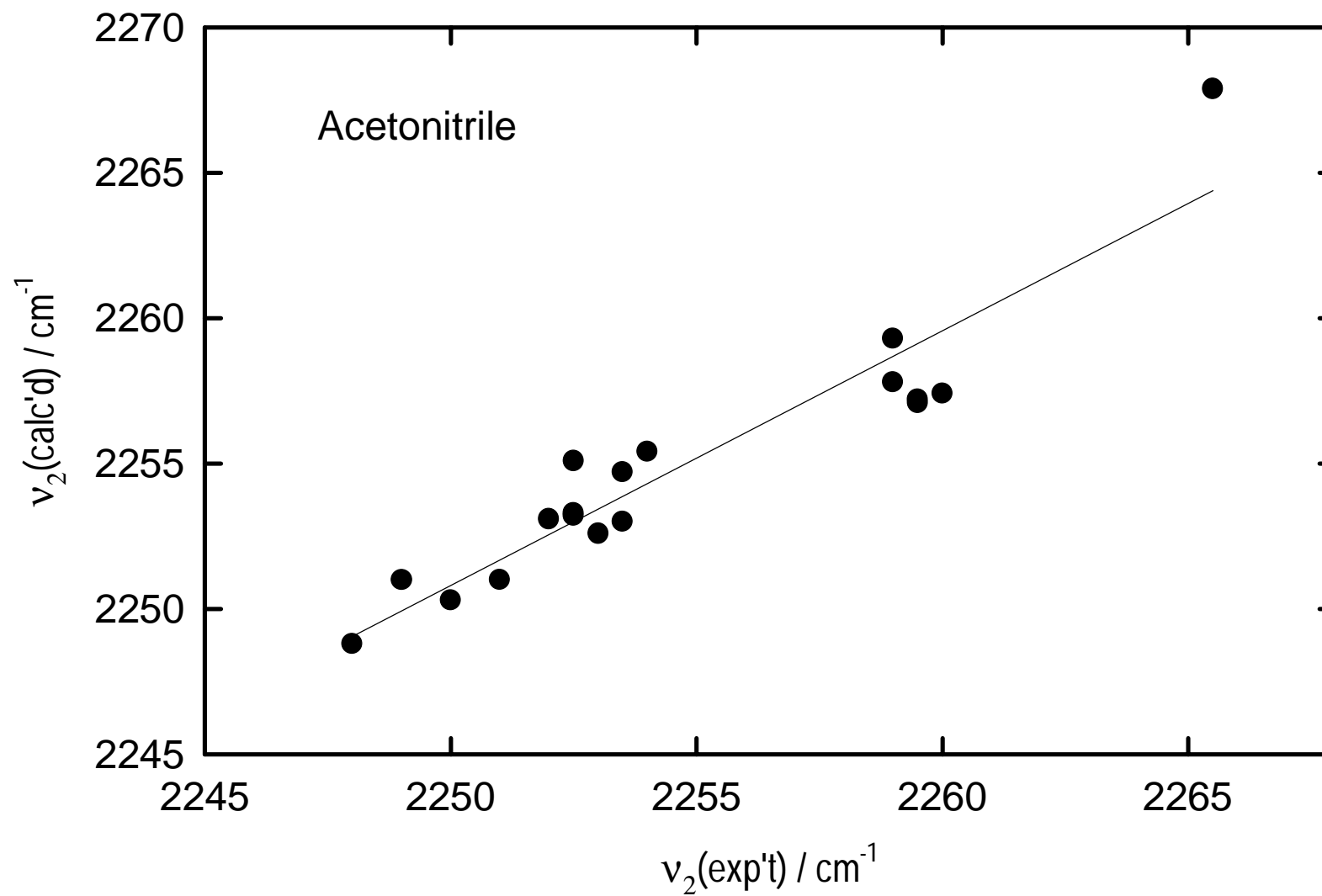
Benzene	0	2.28	8.2	0.0	0.302	0.293
Carbon Tetrachloride	0	2.24	8.6	0.0	0.286	0.273
Chloroform	1.15	4.90	23.1	4.0	0.565	0.265
Dichloroethane	1.86	10.36	16.7	0.0	0.758	0.265
Diethylether	1.15	4.34	3.9	19.2	0.524	0.215
Hexane	0.09	2.02	0	0.0	0.250	0.230
Methylene Chloride	1.14	8.93	20.4	1.6	0.726	0.254

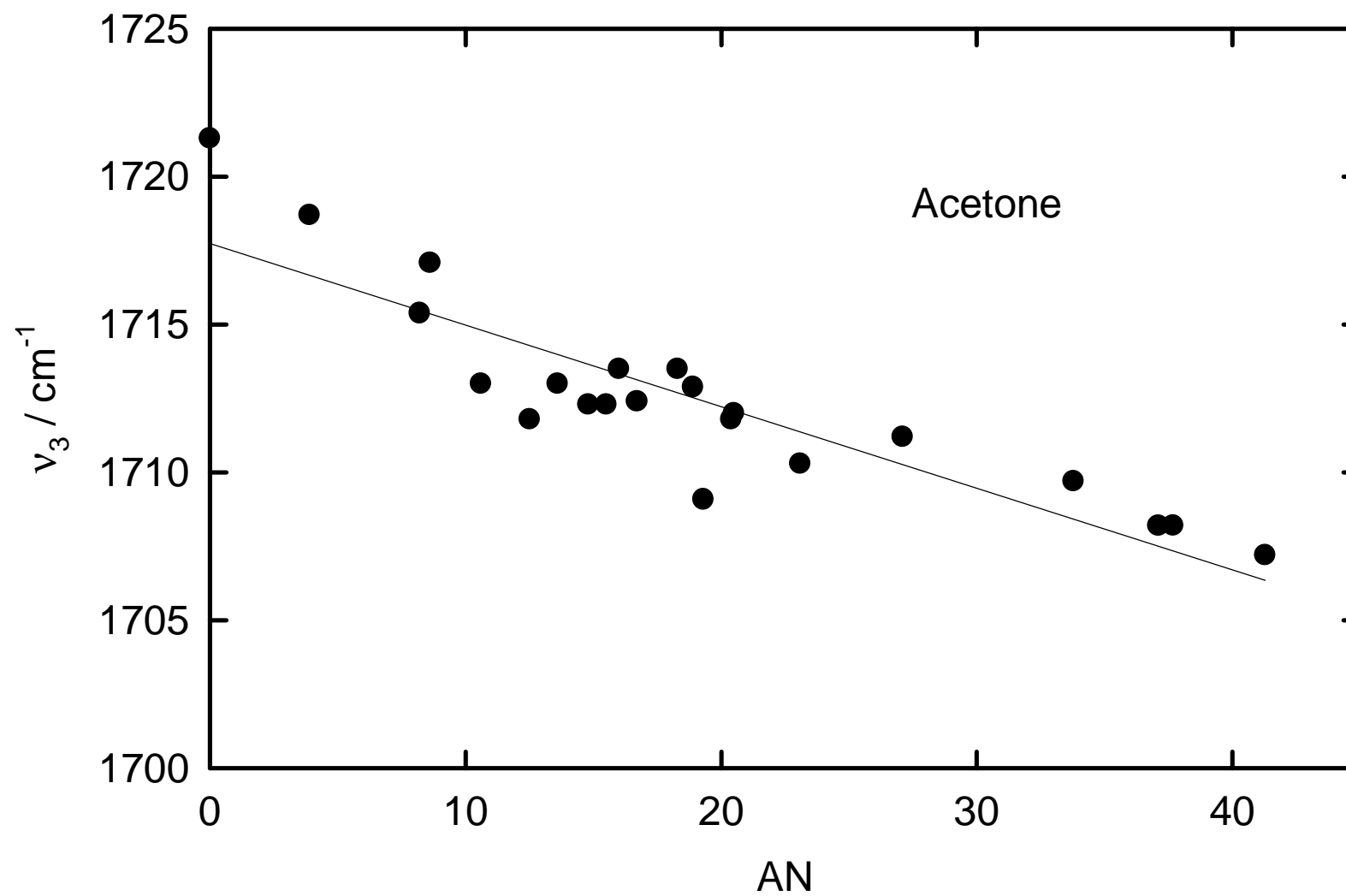
\* 1 Debye =  $3.336 \times 10^{-30}$  Cm

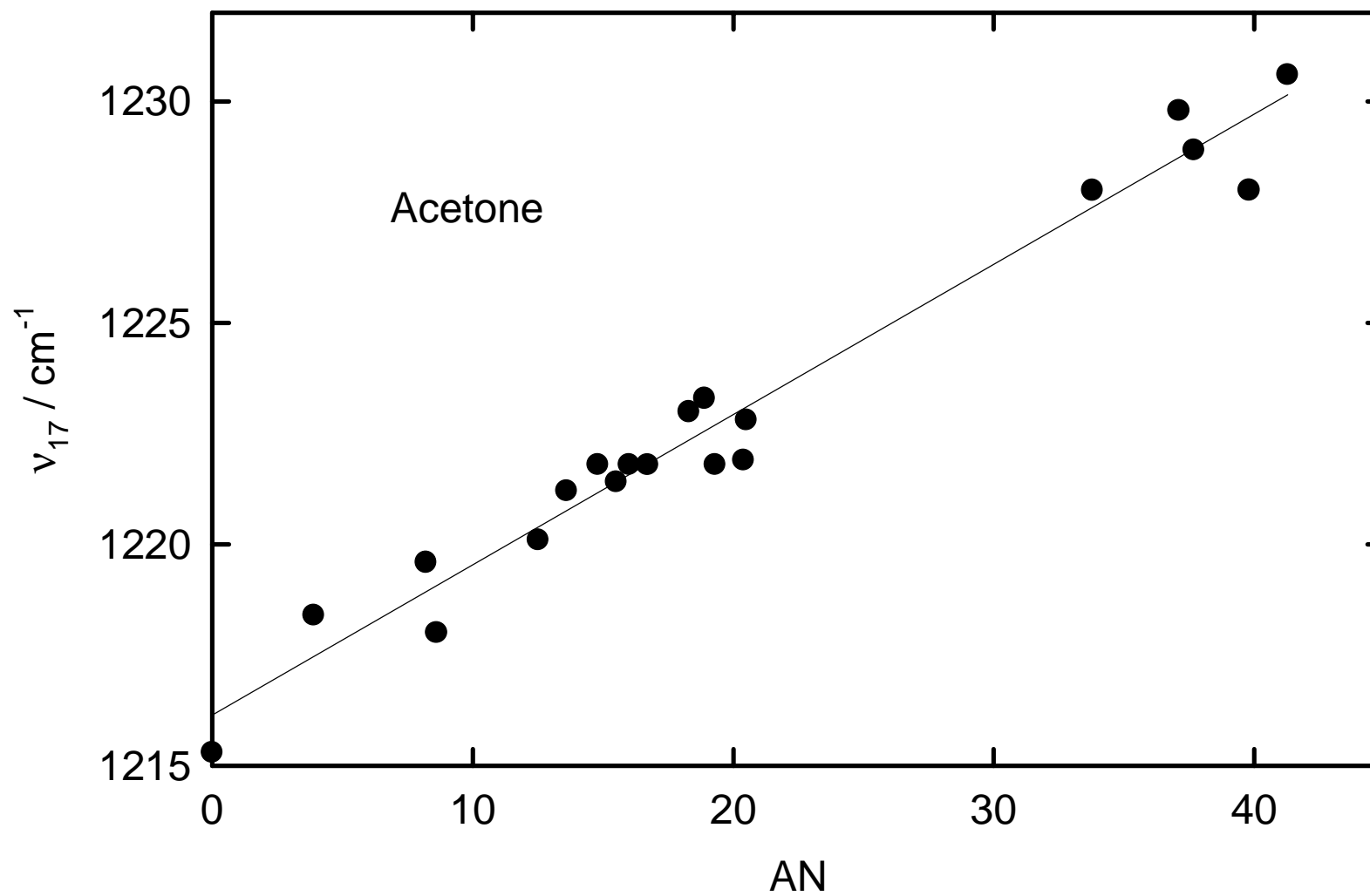
## Legends for Figures

- Figure 1      Plot of the frequency of the  $\nu_2$  band of acetonitrile calculated according to equation (6) against the experimentally observed value.
- Figure 2      Plot of the frequency of the  $\nu_3$  band of acetone as a solute against the acceptor number AN of the solvent.
- Figure 3      As in Figure 2 but for the  $\nu_{17}$  band of acetone.
- Figure 4      As in Figure 2 but for the  $\nu_3$  band of dimethyl sulfoxide.
- Figure 5      As in Figure 2 but for the  $\nu_{17}$  band of dimethyl sulfoxide.
- Figure 6      As in Figure 2 but for the  $\nu_1$  band of propylene carbonate.
- Figure 7      As in Figure 2 but for the  $\nu_5$  band of propylene carbonate.









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